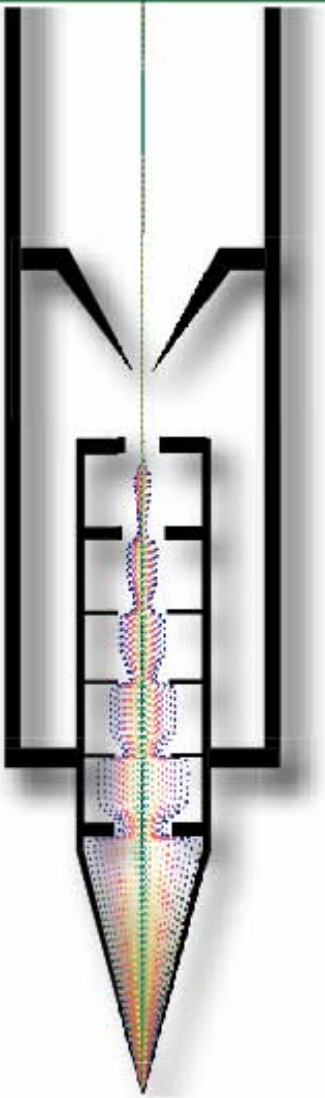
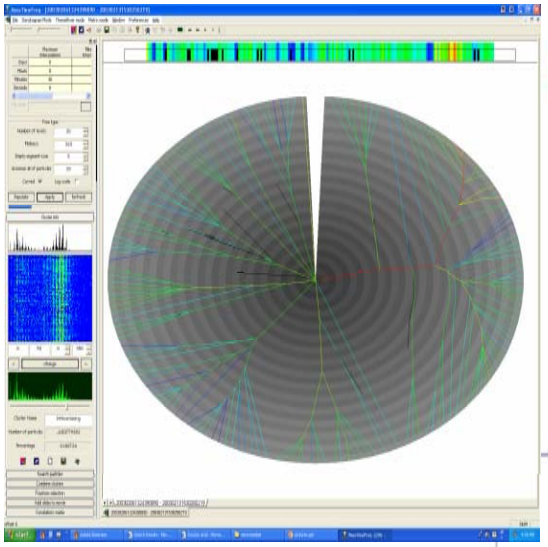
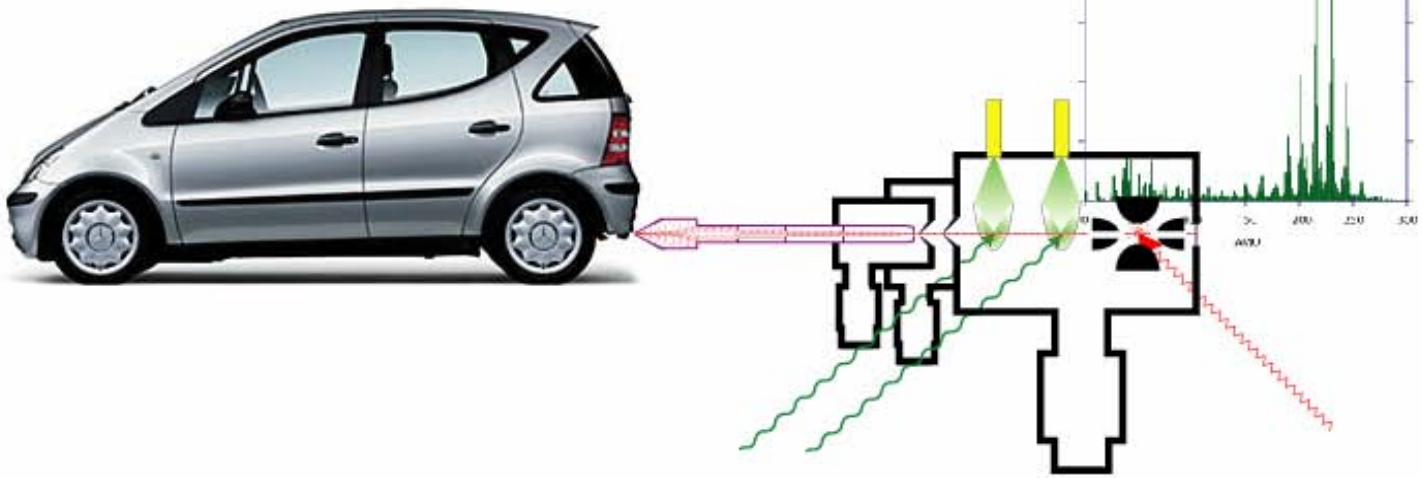
Real Time Tailpipe Emission Measurements



D. Edwards, S. Huff,
S. Lewis, J. Storey

ORNL/NTRC

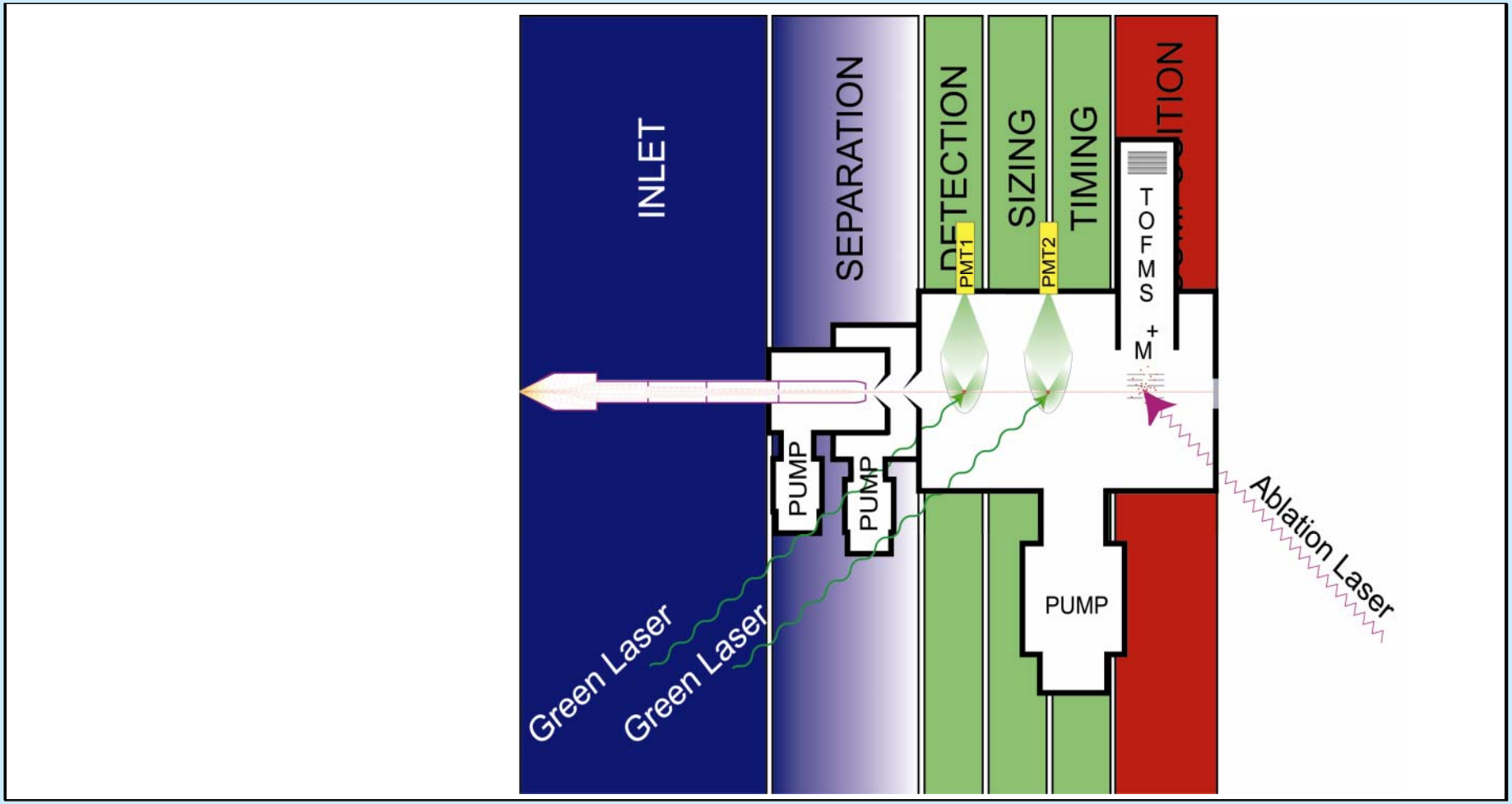




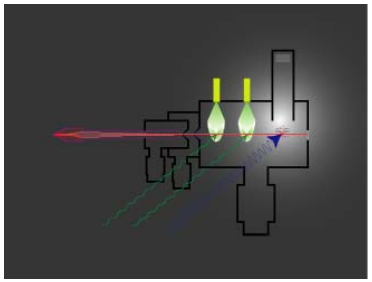
OUTLINE

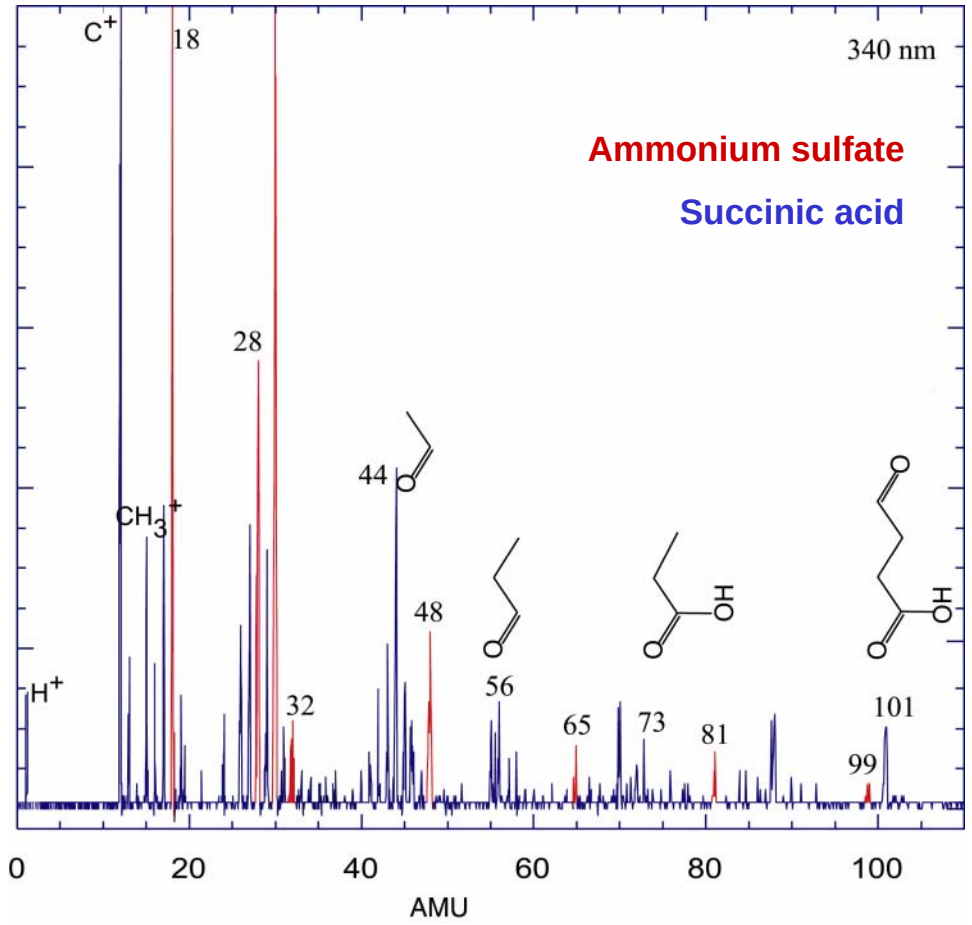
- Single particle mass spectroscopy
- Data mining and visualization
- Results from NTRC on a 1.7L Mercedes Diesel Engine
- Future instrument SPLAT II
- Going back to NTRC

Single Particle Mass Spectrometry: Basics

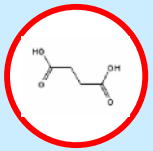


SPLAT-MS can identify different components of mixed aerosol

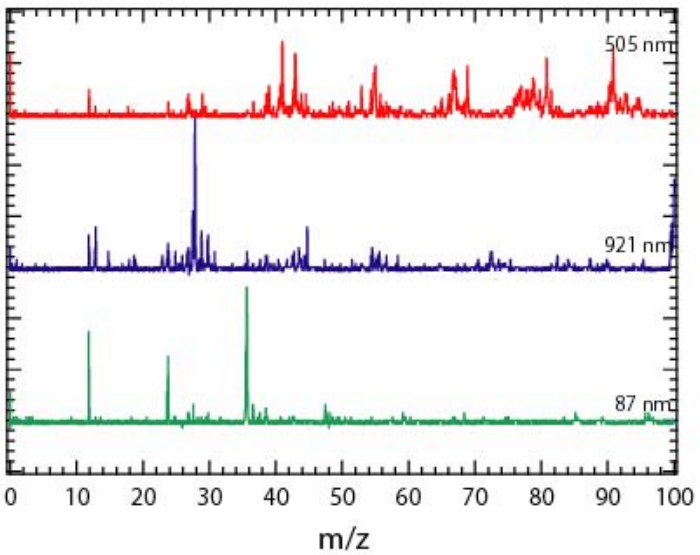




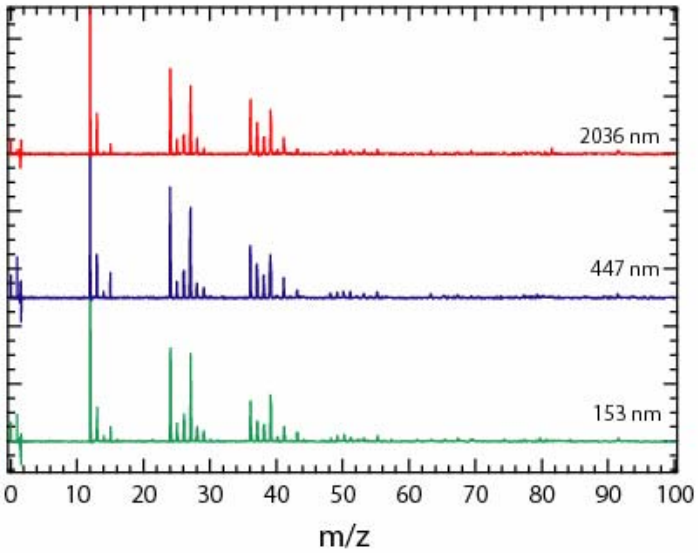
Separating Ablation into Evaporation Followed by Ionization Greatly Improves the Spectra



PURE SUCCINIC ACID PARTICLES

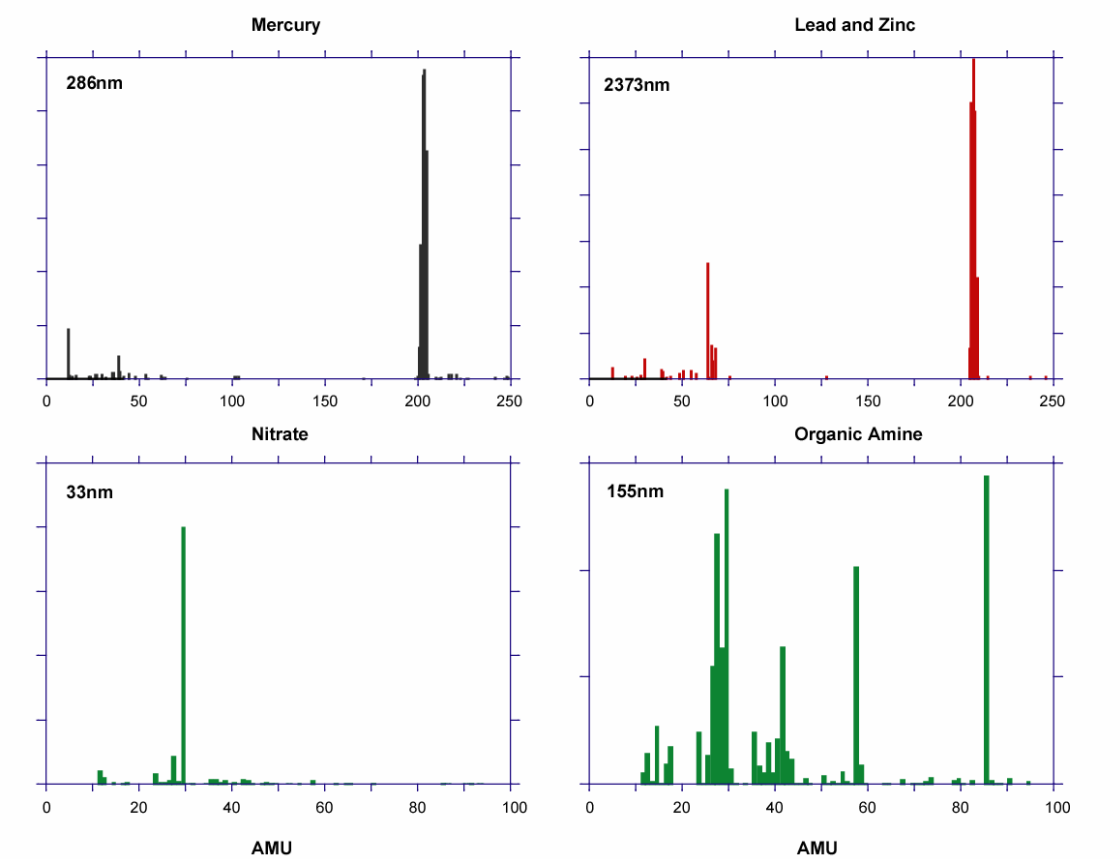


Excimer Laser Only

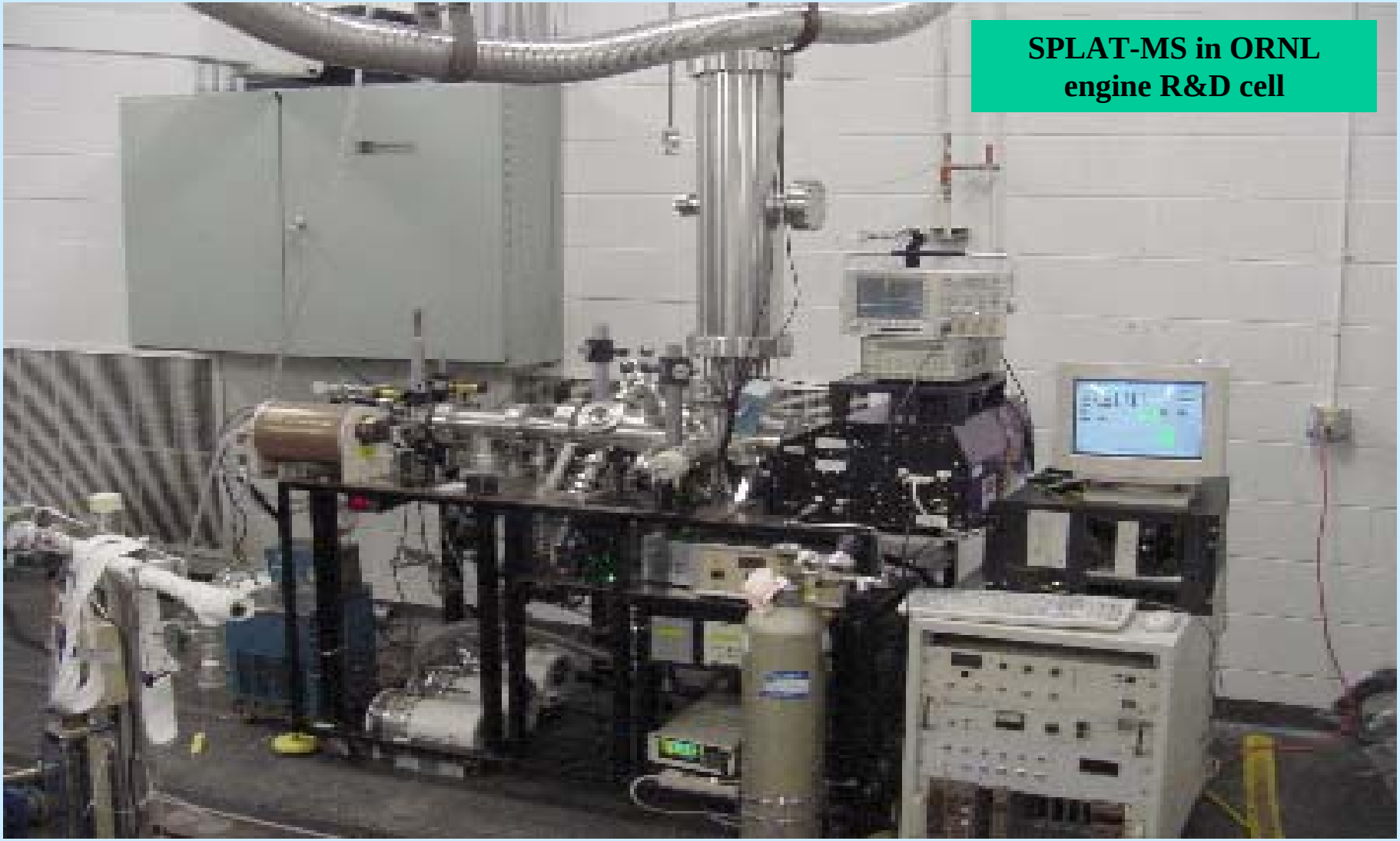


CO_2 and Excimer Laser

4 little Particles from Oak Ridge

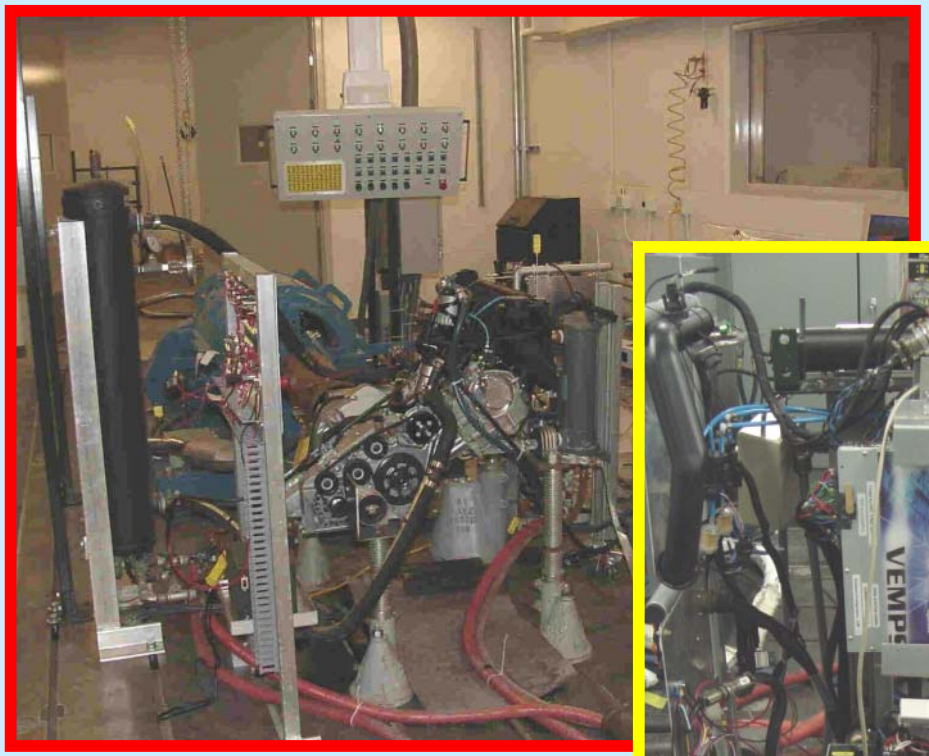


A Study of LD Diesel at ORNL with SPLAT-MS Feb. 2003



Mercedes Engine and Motoring Dynamometer at NTRC Cell 2

New Mercedes 1.7L and motoring dyno



Full-Pass Controller
Developed with Ricardo

Control Room

Summary of the Experiments

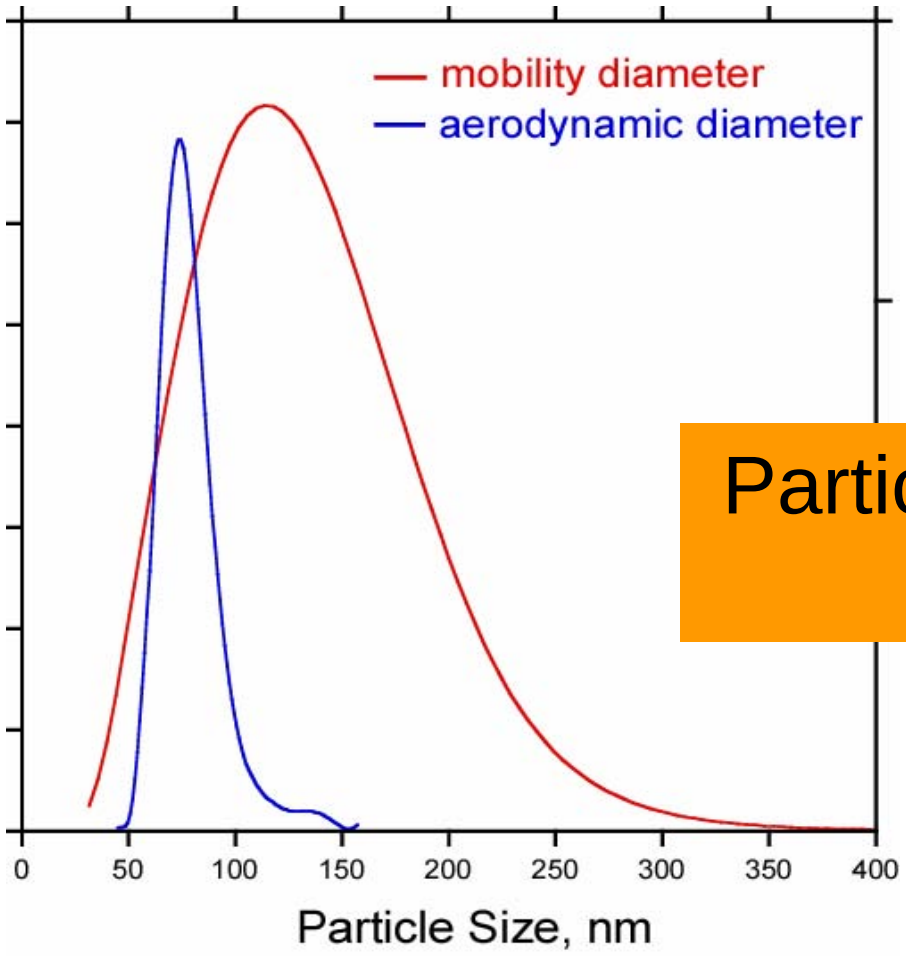
- Measurements of exhaust particle size, density and composition were performed under variety of operating conditions:
  - Changed loads and RPM
  - LTC/EGR
  - ECD-1 and oxygenate fuels
  - Changed injection sequence and timing
  - Pre and post catalyst
- Acquired spectra for ~500,000 particles – large dataset!
- Used high dilution to avoid sampling artifacts
- Use an IR-UV scheme

Let’s Take a Look at the Data

Peter Imerich

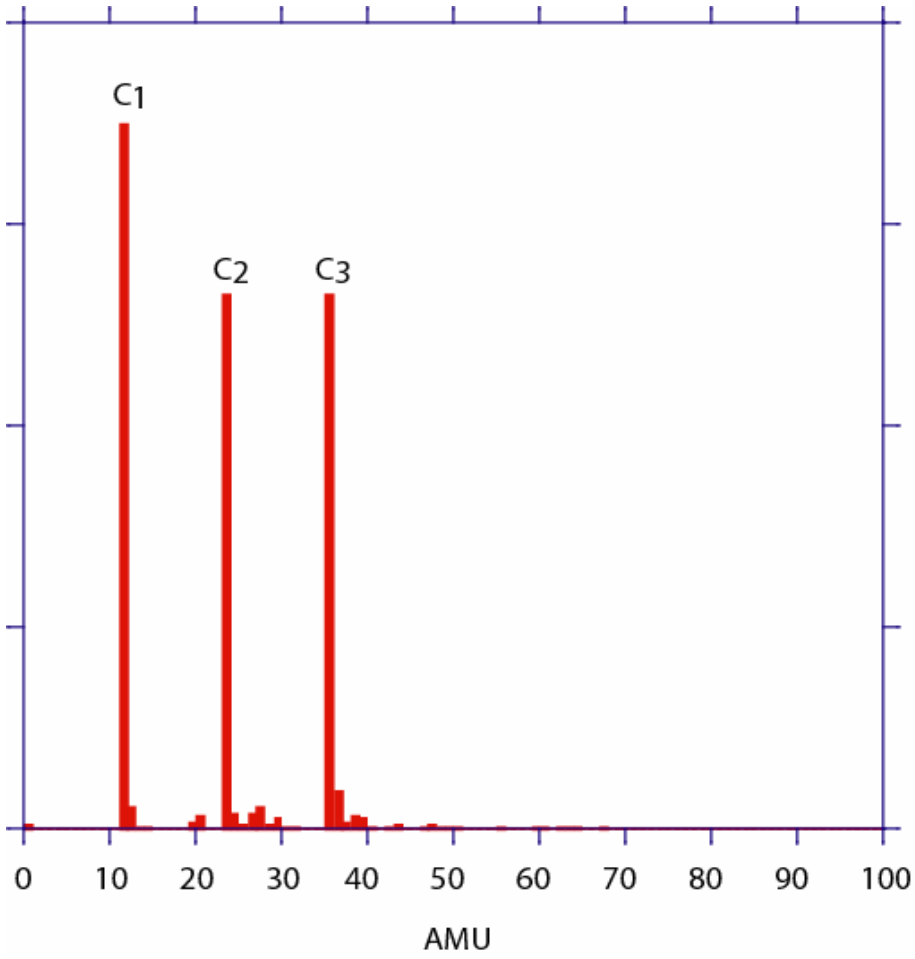
Wei Zhu, Bin Xu, Klaus Muller

The Diesel Exhaust Challenge to Particle-MS

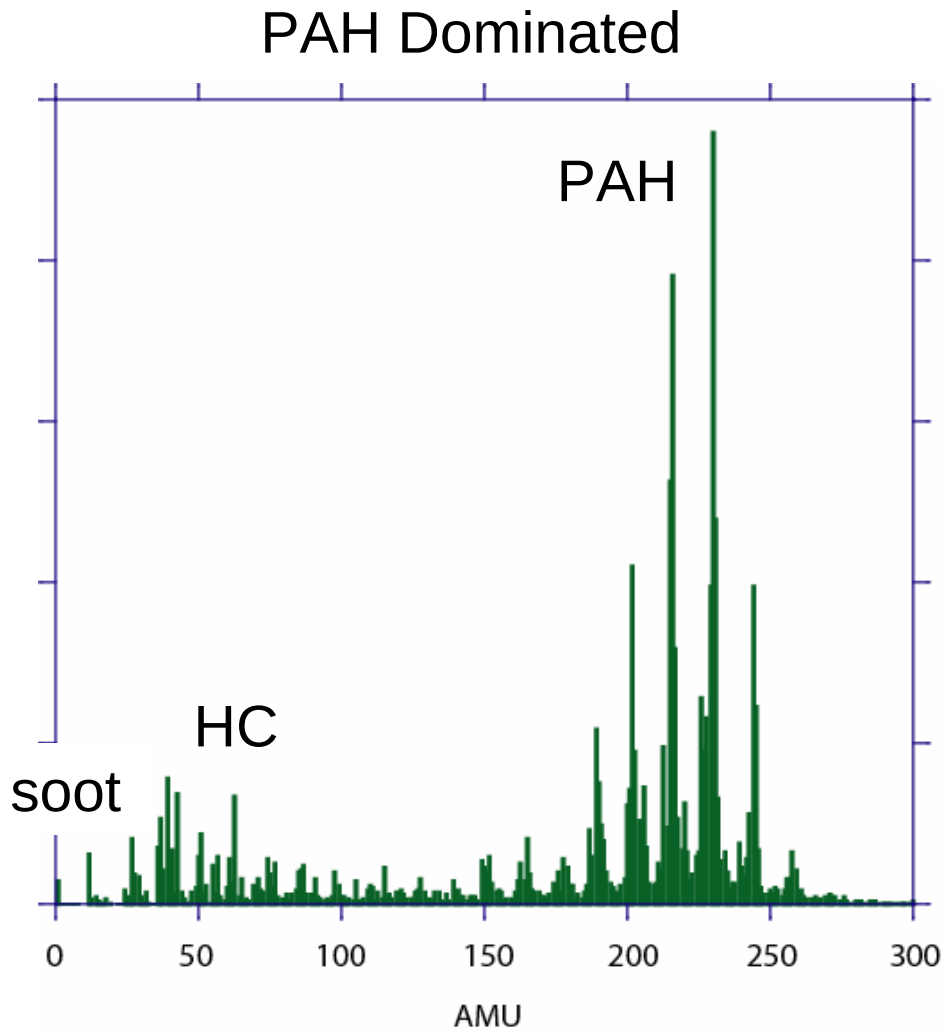


Particles are Very **Small**

Soot Particles are Most Prevalent



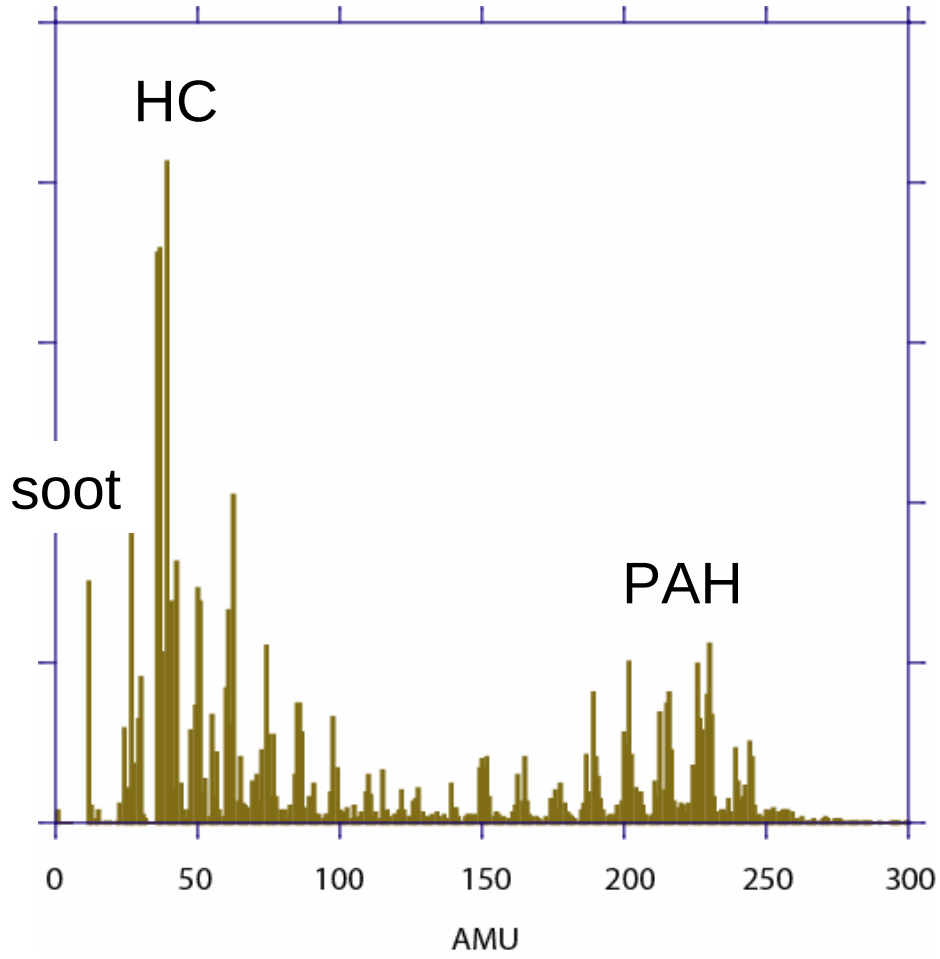
PAHs Volatilize from Particles using Laser Heating



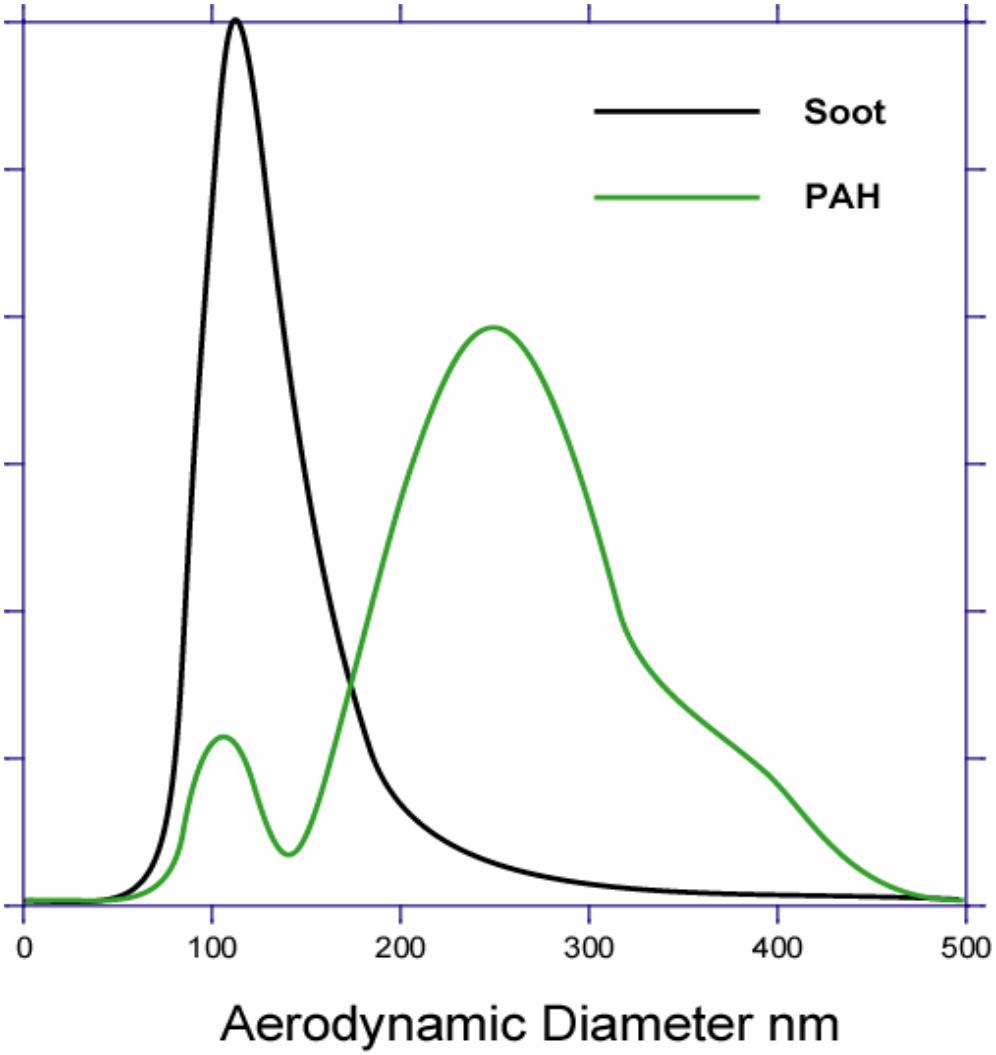
30	NO
152	178-C_2H_2
178	phenanthrene
192	C_1 Alkyl phenanthrene
202	Pyrene
216	Alkyl pyrene
234	C_4 Alkyl phenanthrene
252	Benzo pyrene

Unburned and Partially Oxygenated Fuel Volatilize from Particles using Laser Heating

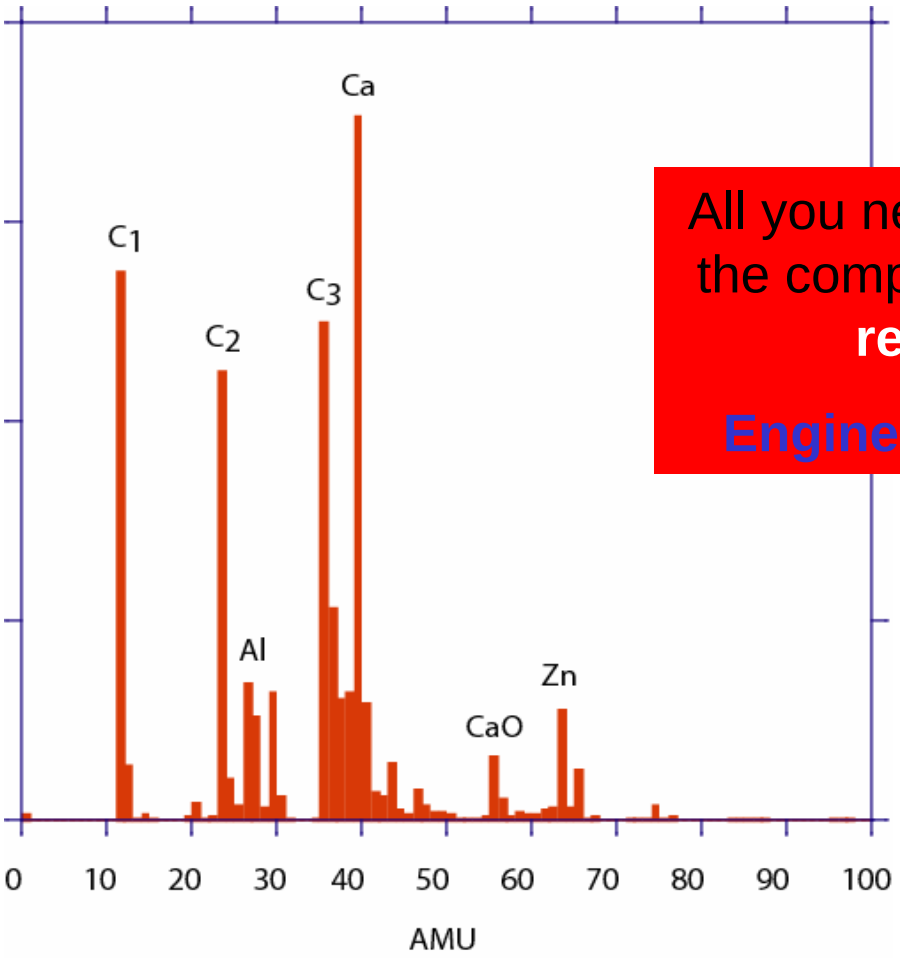
Partially oxygenated hydrocarbons soot and PAH



Where are the PAHs



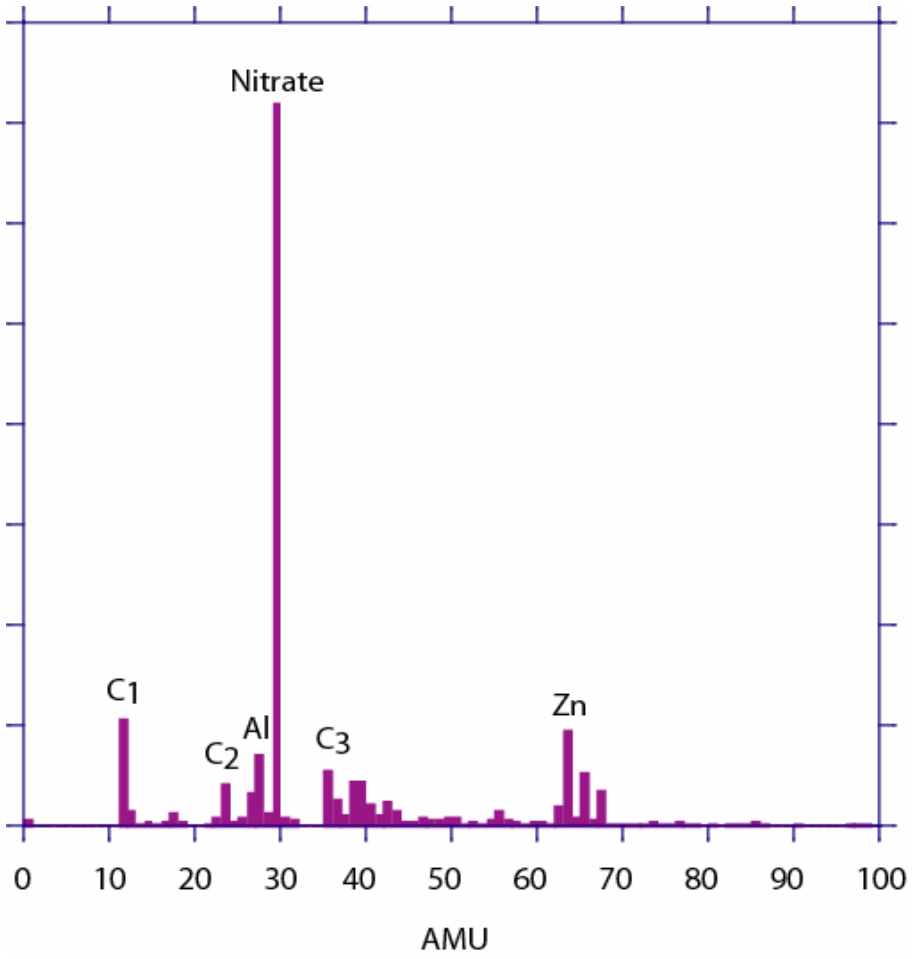
At Rated Speed, Oil Components and Engine Wear and Tear Appear Products Appear in Particles



All you need is to watch the computer screen in **real-time**

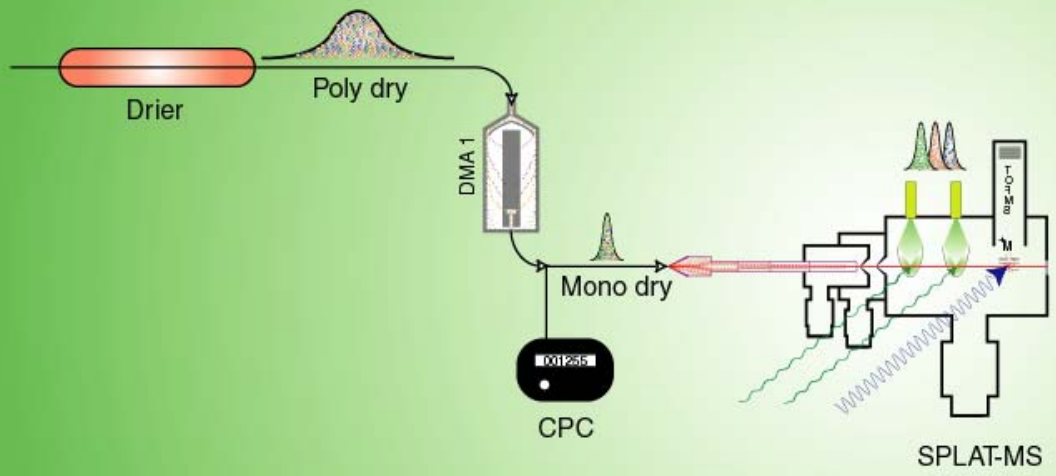
Engine diagnostics

A Small Fraction of Particles Contain Significant Amounts of Nitrates



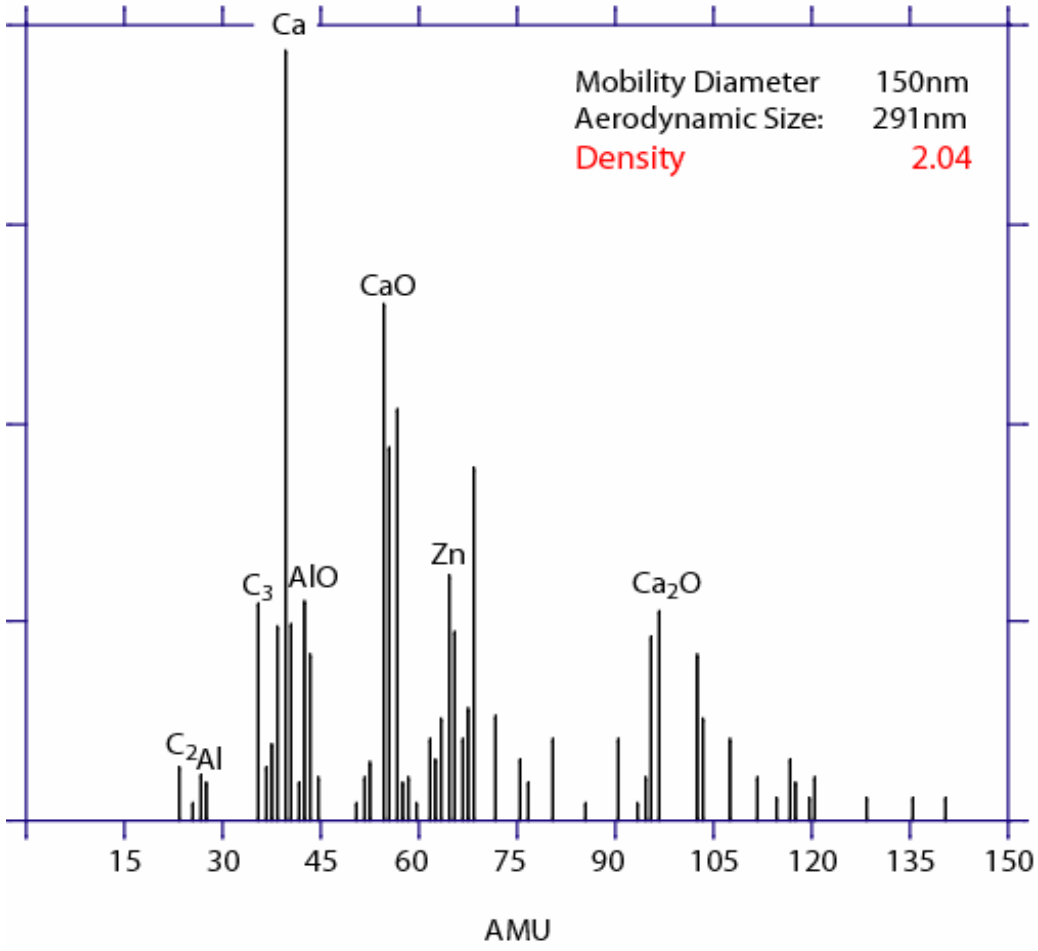
Size, Composition & Density
Using SMPS to Feed Particles to SPLAT-MS

D_{Aero}/D_{DMA}=Density



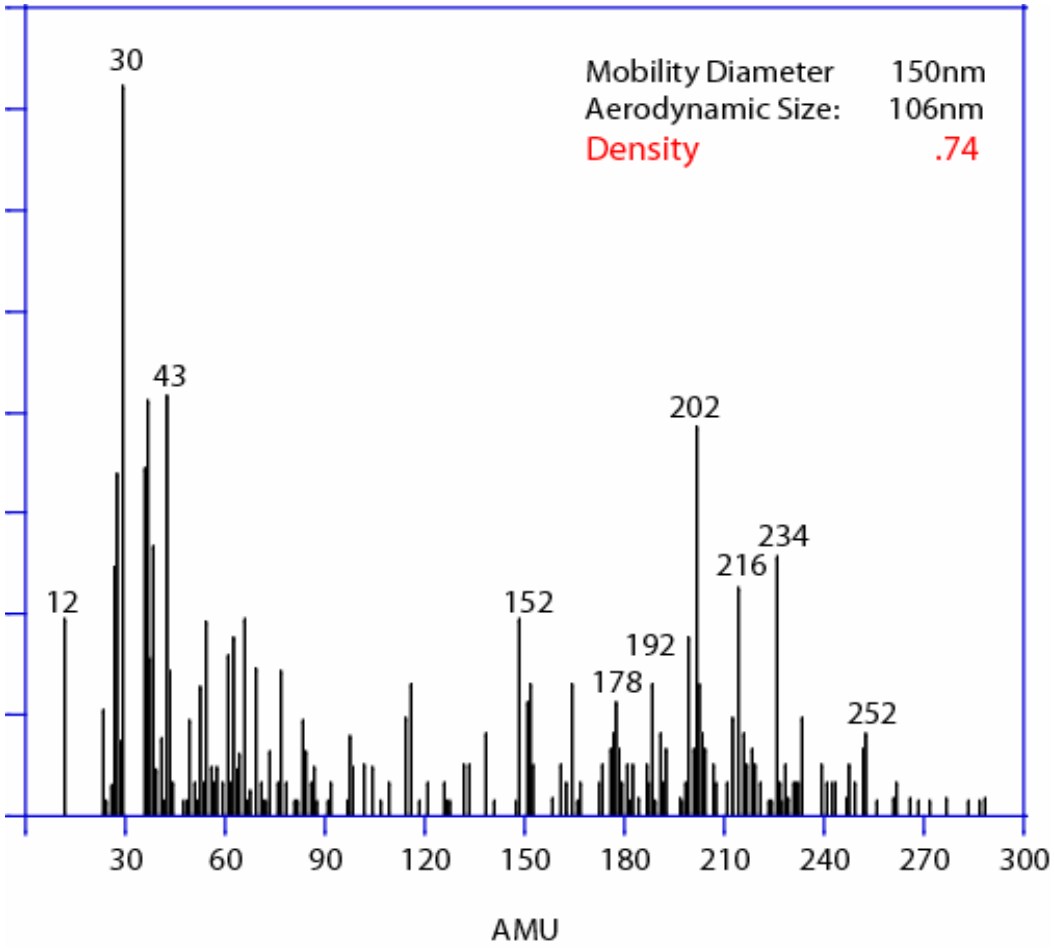
Particle Density Depends on Composition

Lube Components and Engine Wear and Tear



Density Depends on Composition

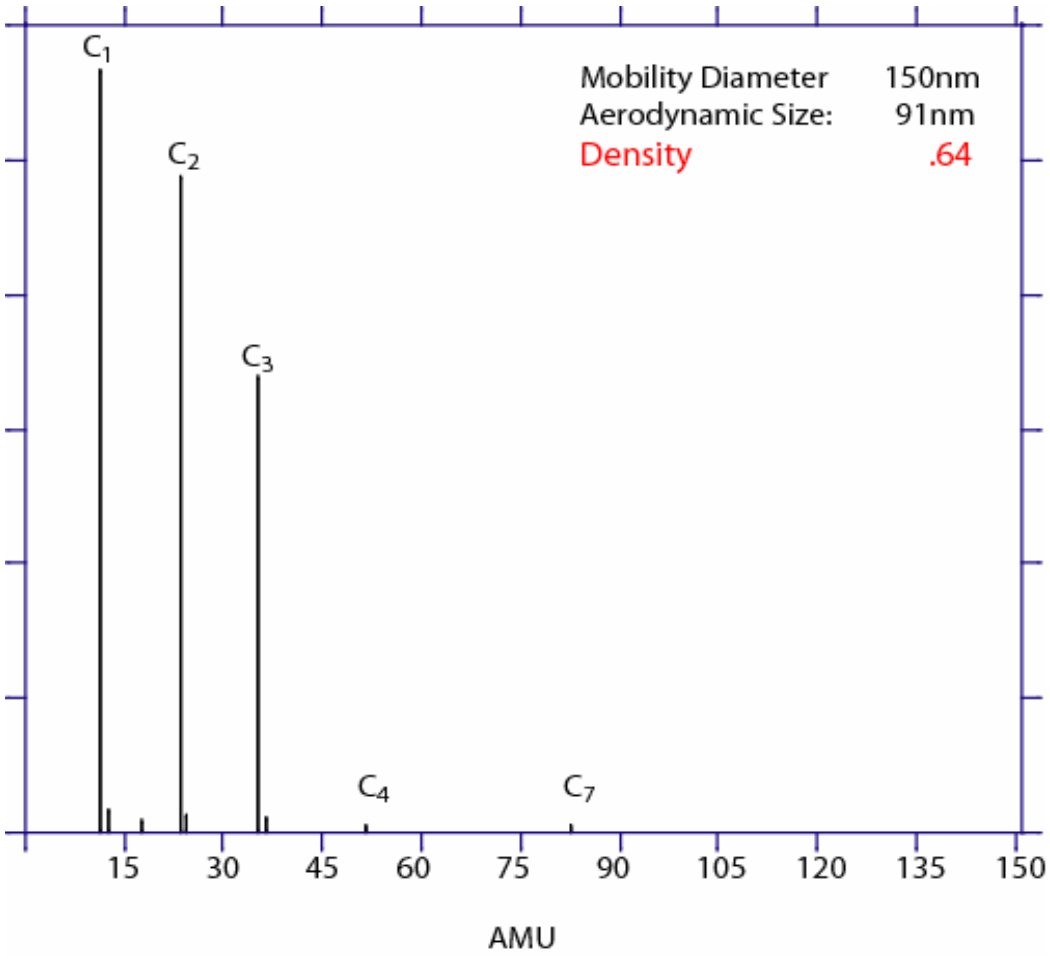
PAHs



30	NO
152	178-C_2H_2
178	phenanthrene
192	C_1 Alkyl phenanthrene
202	Pyrene
216	Alkyl pyrene
234	C_4 Alkyl phenanthrene
252	Benzo pyrene

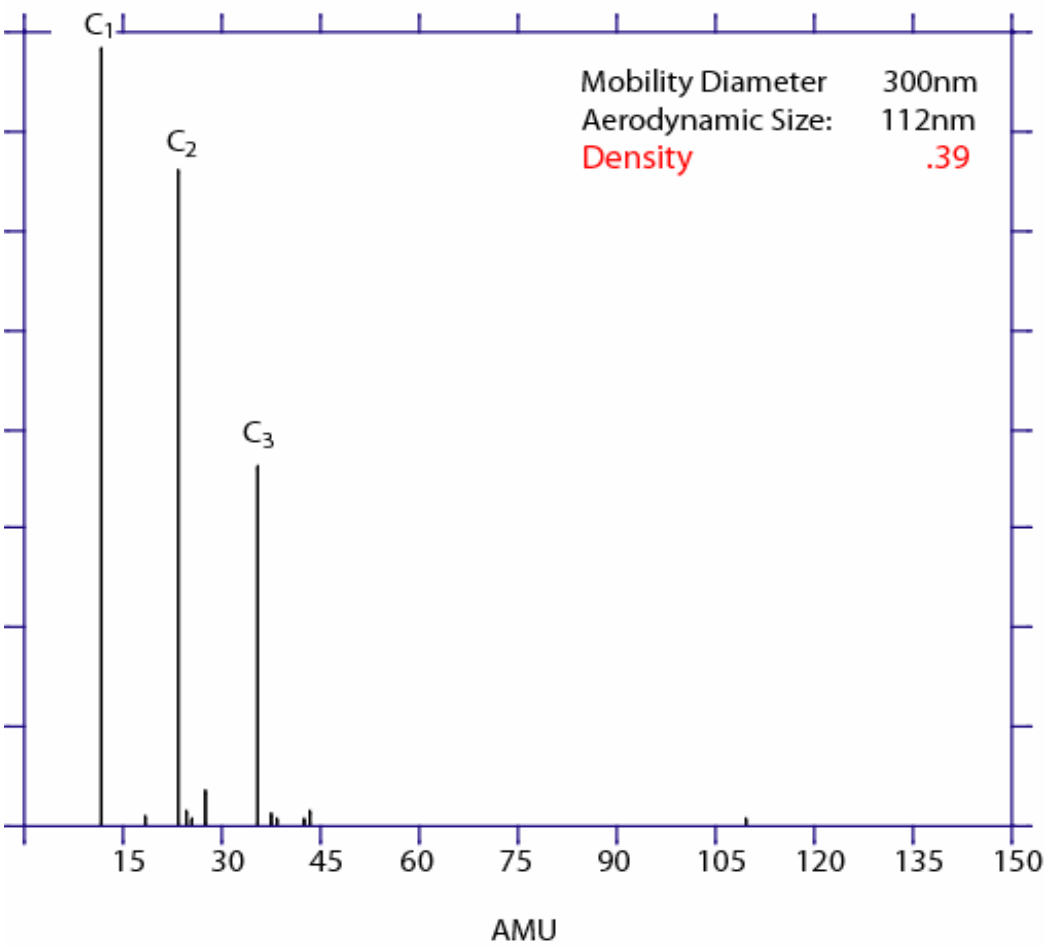
Particle Density Depends on Composition

SOOT

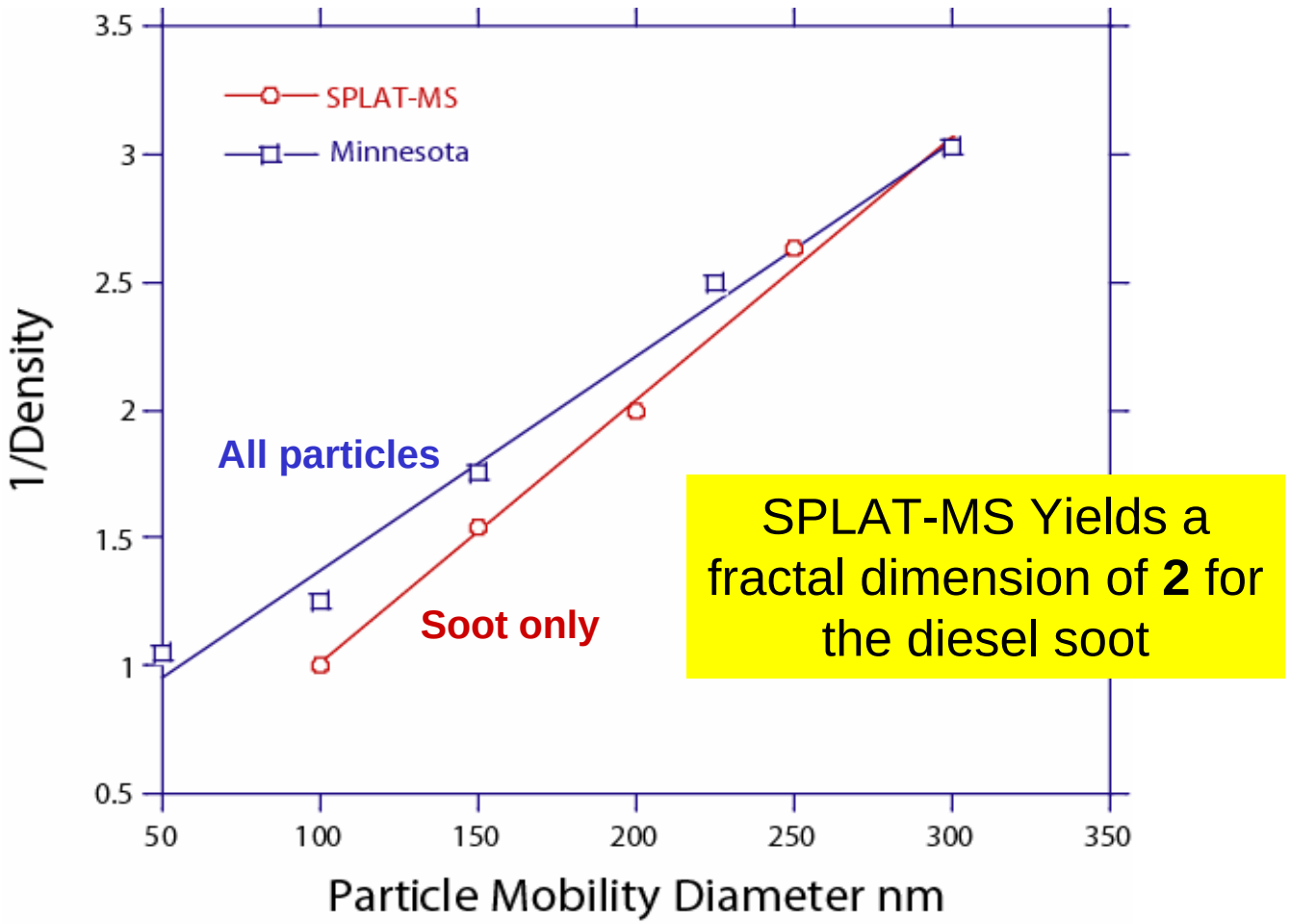


Particle Density Depends on Composition and Size!!

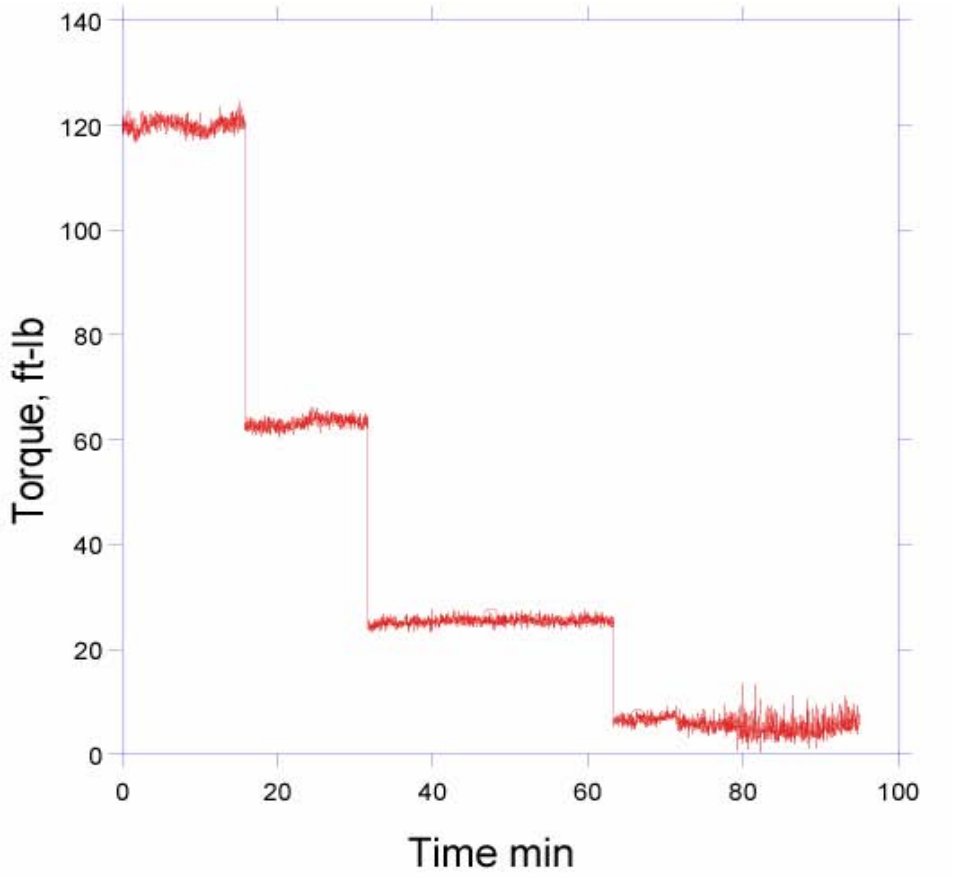
SOOT



Size vs. Density Relationship for Soot Particles



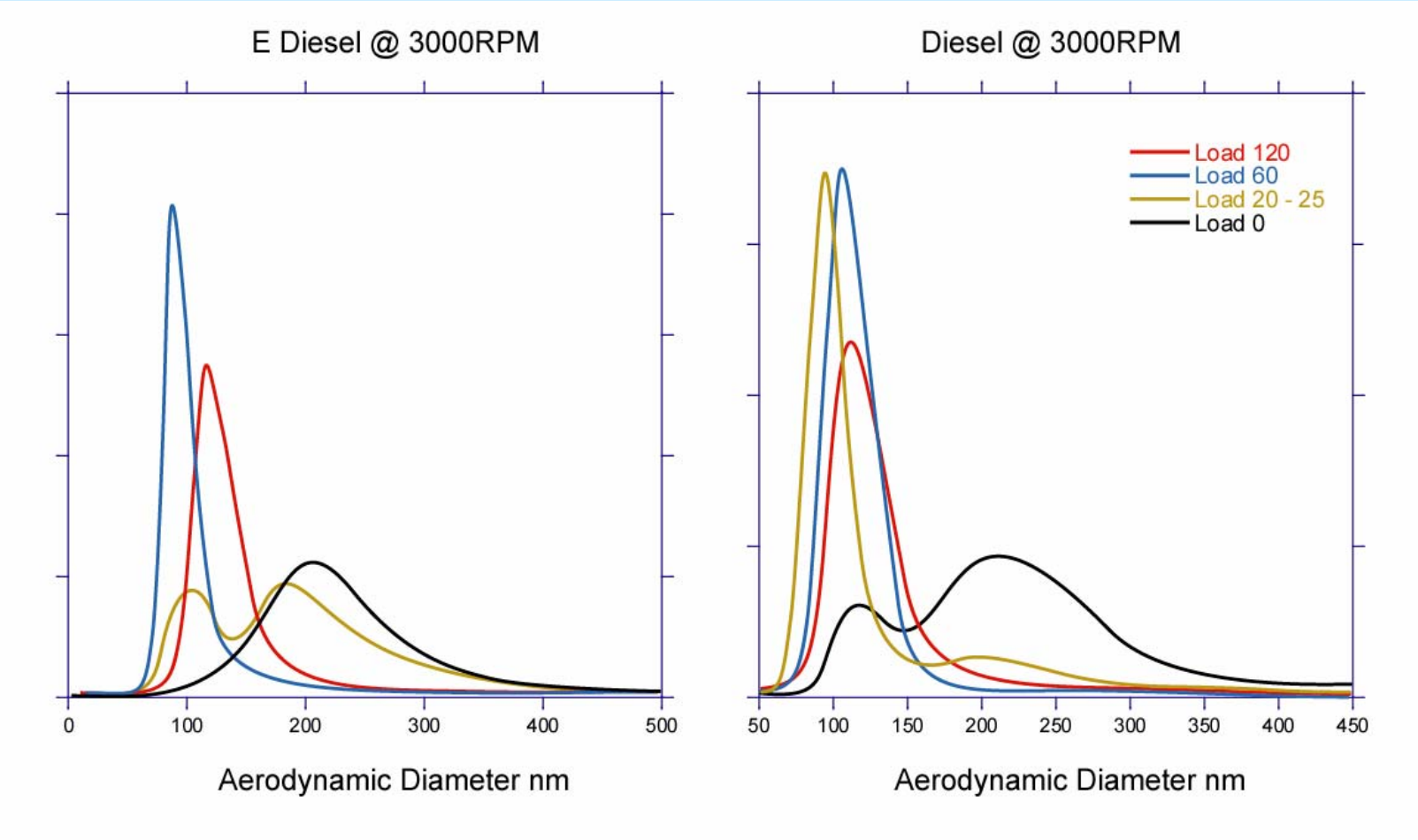
SPLAT-MS Yields a fractal dimension of **2** for the diesel soot



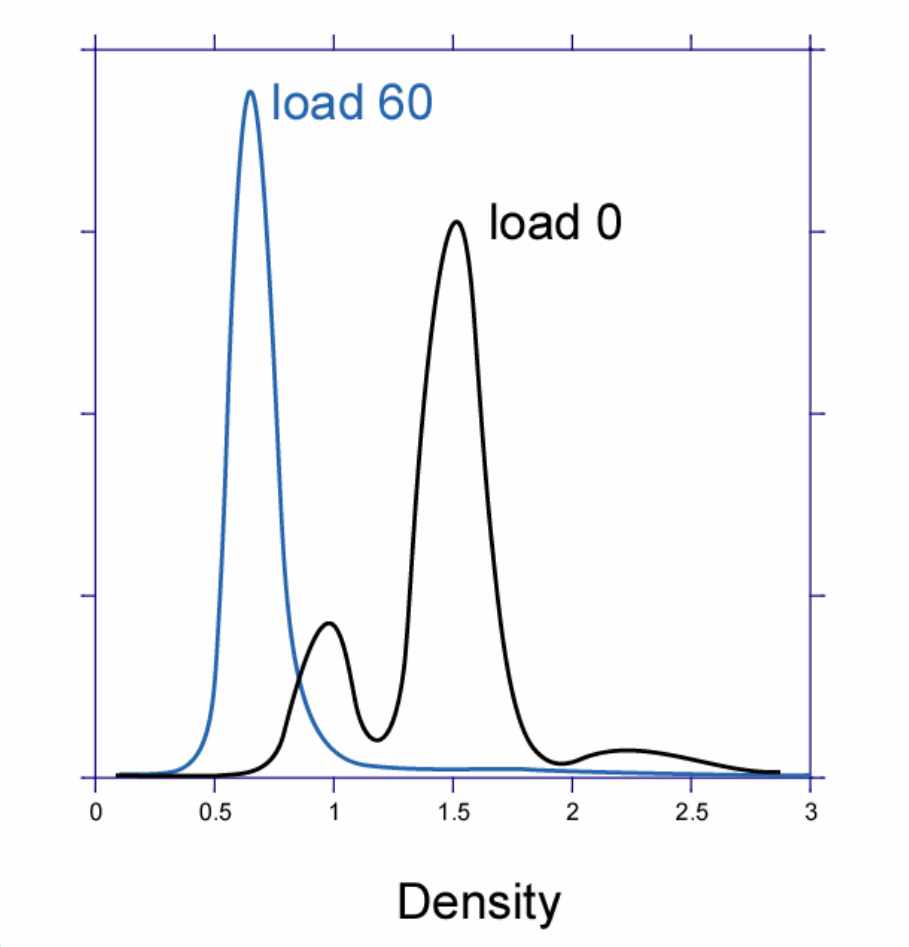
PM Composition and Density as a Function of Load @ 3000RPM

PM as a Function of Load @ 3000 RPM

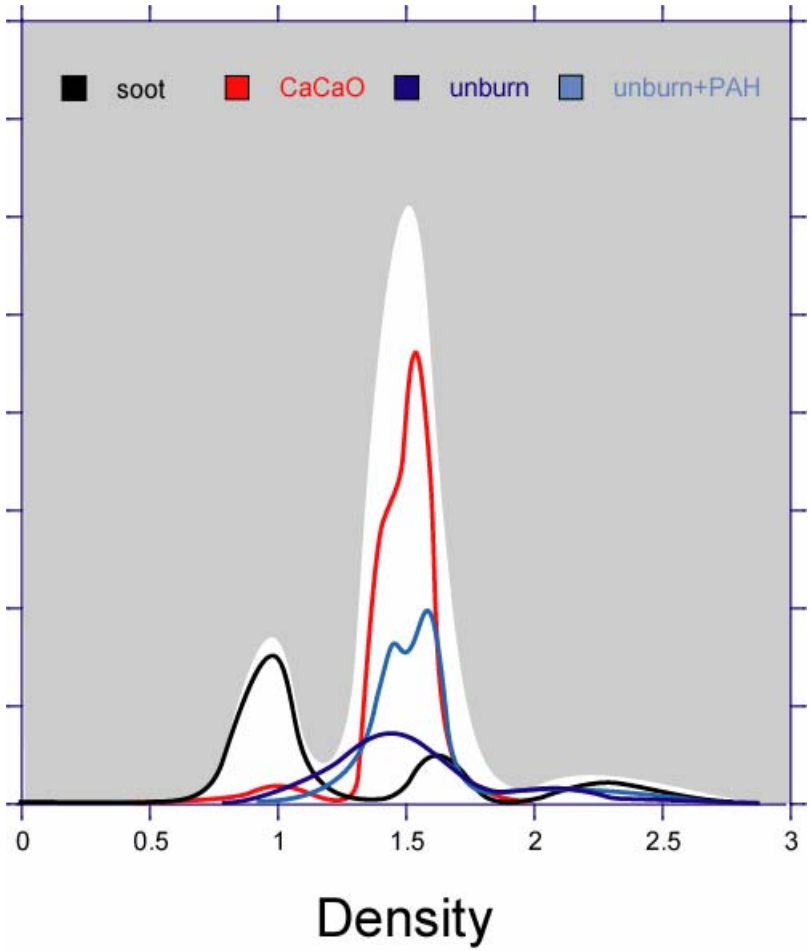
Aerodynamic Diameter



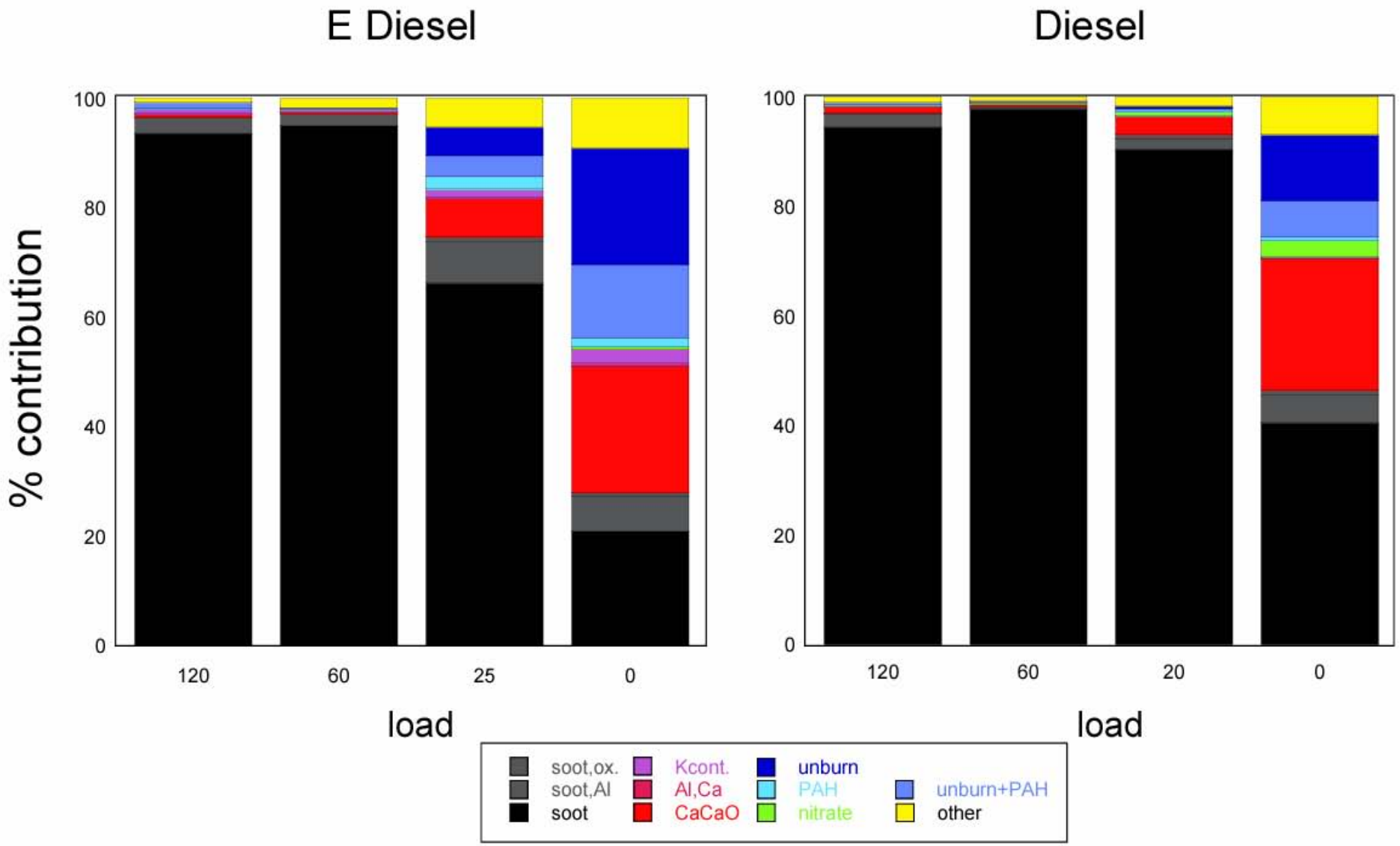
Engine as a Function of Load @ 3000 RPM



Engine as a Function of Load @ High RPM

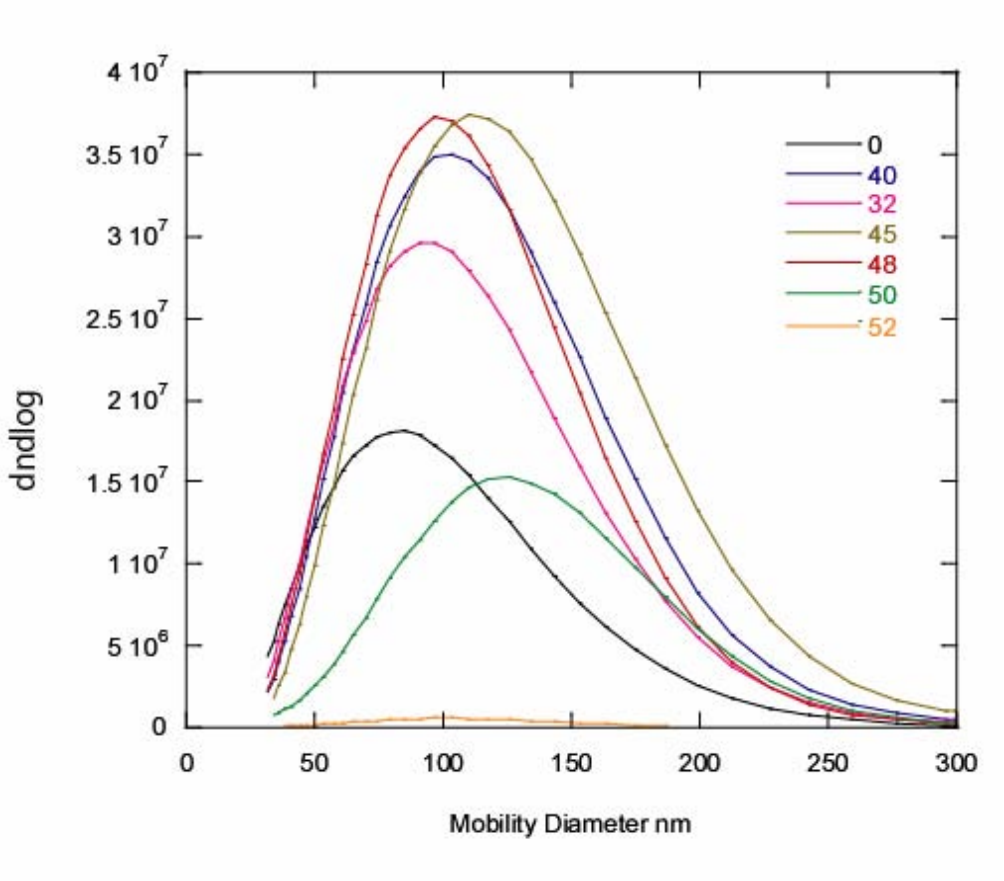


Engine as a Function of Load @ High RPM

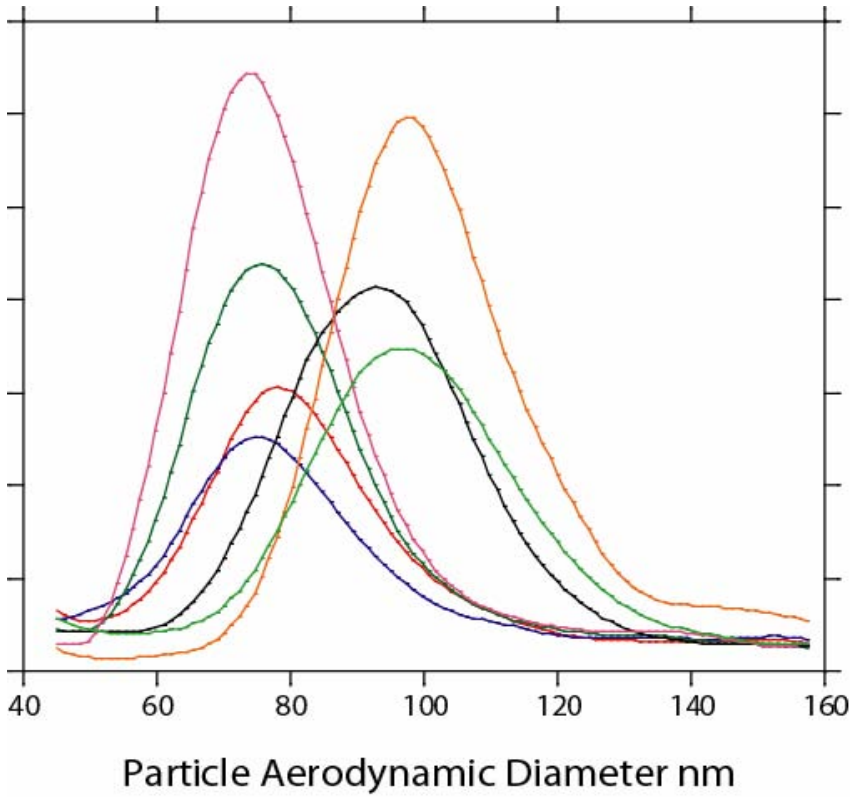


Particle Number Concentration and Size vs. EGR

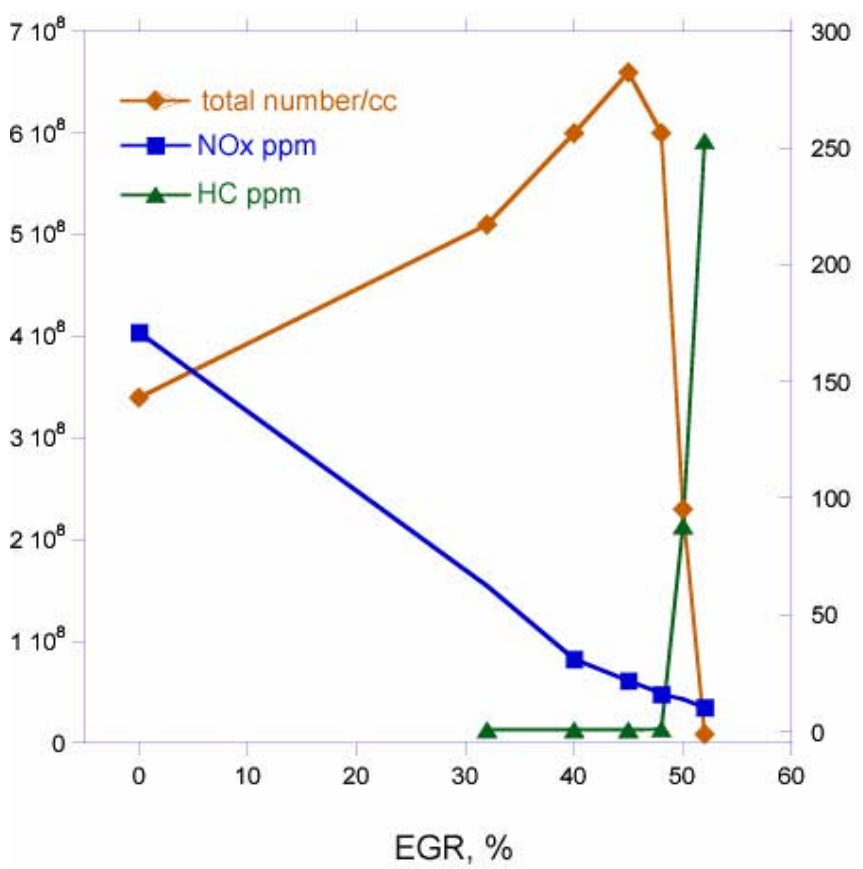
Mobility size distributions

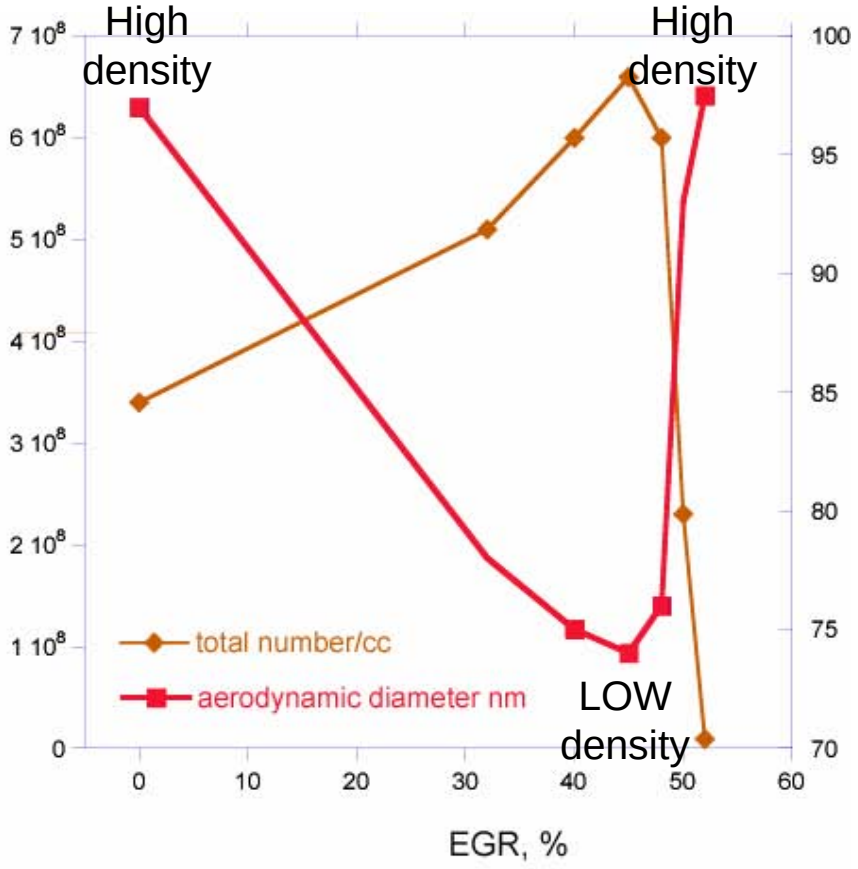


SPLAT size distributions



Particle Number Concentration and Aerodynamic Size vs. EGR



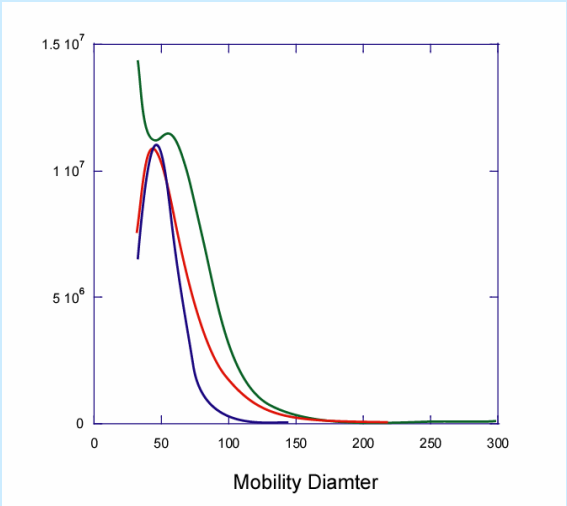


Where Do we Go From Here

SPLAT II

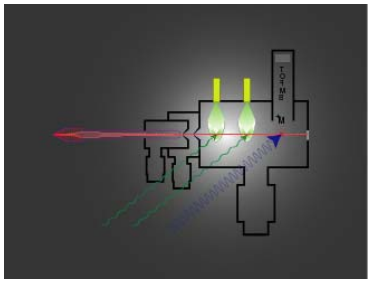
Where do We Go From Here: The New SPLAT

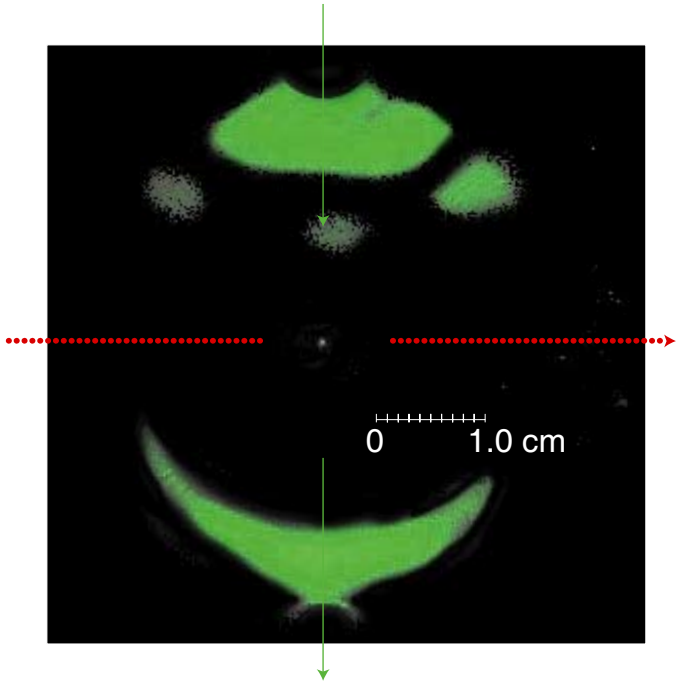
Smaller particles (30nm)

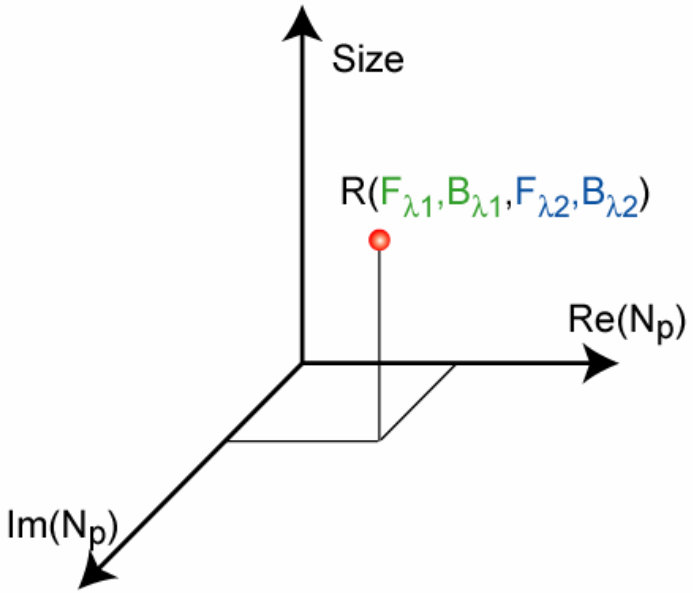


Replace the Green laser with UV

Effective Density, and Optical Properties Without DMA

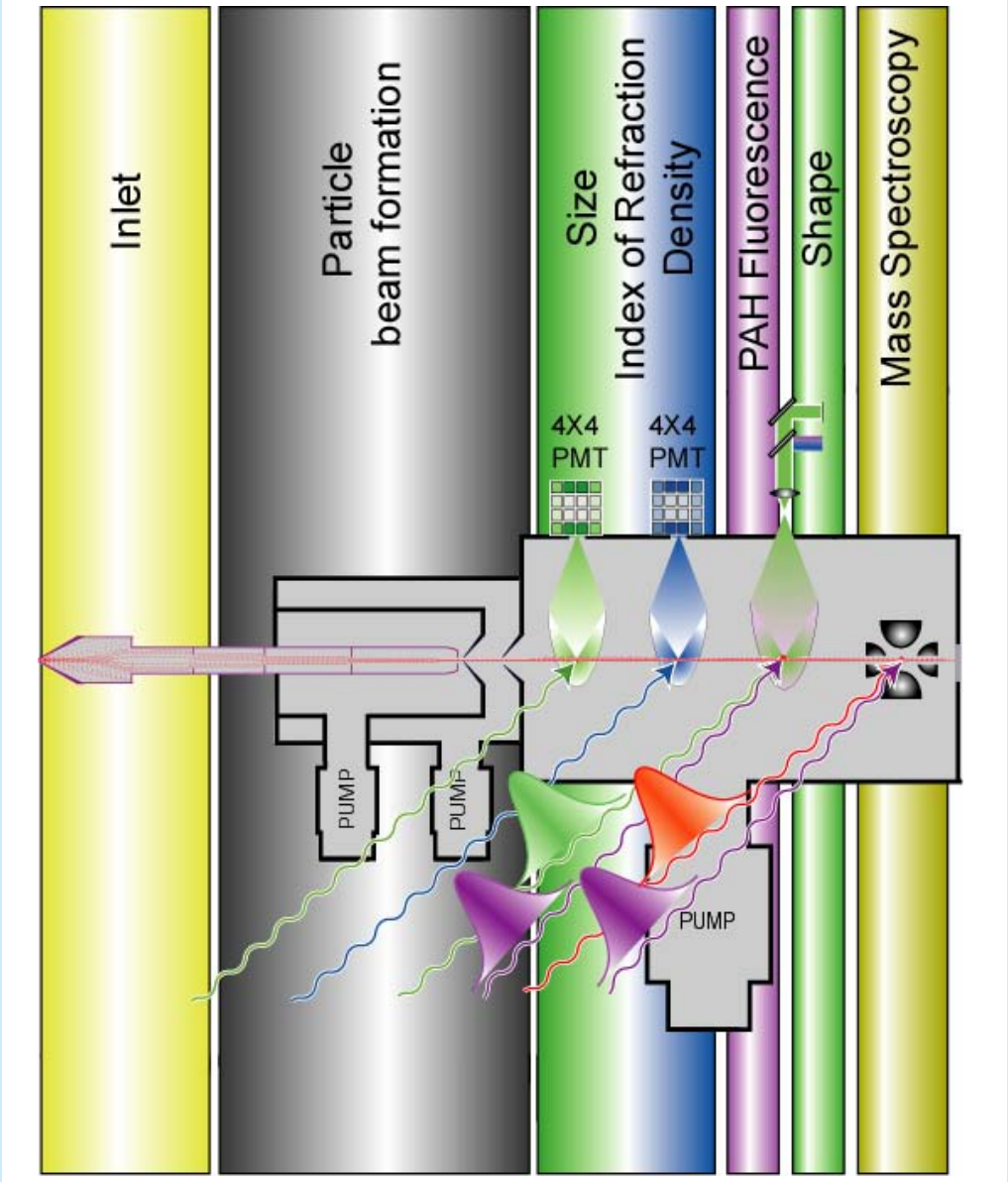




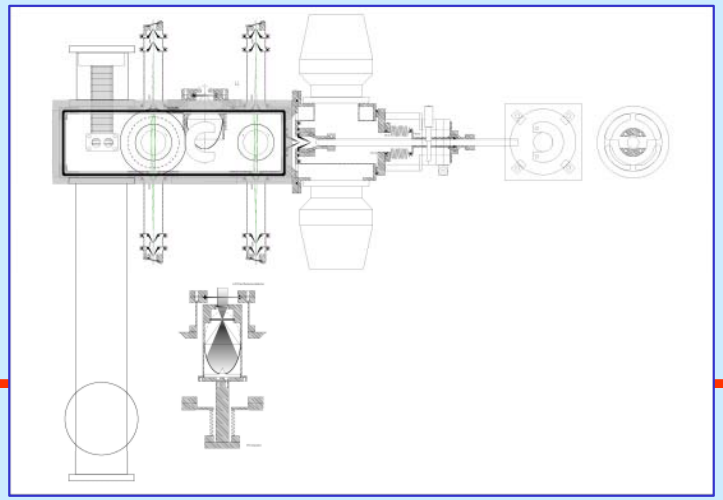


Two color angle resolved light scattering (Zsymanski et al. 2002)

New SPLAT



1. **Aerodynamic size**
2. **Index of refraction**
3. **Density**
4. **Shape**
5. **Incandescence (soot)**
6. **Composition IR + UV**
7. **Composition IR + Cl**



Tailpipe Emissions Comprehensive Characterization

Going Back to NTRC

- **SPLAT -** Single particle, size,composition, optical properties, density
- **AMS -** Semi-volatile in particle phase size resolved
- **SEM-** Single particle microscopy, composition, chemistry
- **Cell Exposure -** Proteomics

Conclusion

- SPLAT-MS provides in real-time individual particle:
  - Size – 40nm to 3micron
  - Composition - IR evaporation followed by UV ionization
  - Density – size and composition resolved
- SPLAT-MS makes it possible to monitor engine performance in real-time by watching the computer screen
- SpectraMiner is a powerful tool for detailed data analysis
- All particles are internally mixed but there are clear classes
- Particle size, and composition are a strong function of engine operation
- Density of soot is inversely proportional to size
- Non soot particles have higher aerodynamic diameter
- PAHs are found in particles with unburned fuel, and with soot